

CHEMICALS FROM COAL

by

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This paper is intended as a review up to 1962 of the history of chemicals from coal, the controlling influences in the past, and what may be expected in the future. The term "chemicals" covers primarily ammonia, the light aromatics (benzene, toluene, and xylene), tar acids, tar bases and tar or pitch, gas, and coke.

In the United States, these chemicals have been derived from coal almost exclusively through high-temperature byproduct carbonization. In England and in Europe, these and other chemicals have been obtained to some extent through various low-temperature carbonization processes and by coal hydrogenation in England and Germany for a few years. No attempt will be made to trace the periodic efforts to establish low-temperature carbonization in the United States. In no case did these result in significant commercial chemical production.

In this country, the production of coke was closely linked to the demands of the iron and steel industry. Up to the time of World War II, in periods of high industrial activity with good markets for steel, coke-oven capacity and output increased and the coal chemicals were in good supply. When demand for steel decreased, oven operation slowed down and the supply of chemicals fell also. Markets for the chemicals other than coke were never strong enough to justify oven operation for these alone.

In 1910, coke-making capacity amounted to about 70 million tons per year--substantially all in beehive ovens with no chemicals recovery. Coal tar derivatives were obtained primarily by importation from Germany. During and immediately after World War I with the German supplies cut off, the markets for chemicals obtainable from coal were strong enough to support the construction of byproduct ovens and start the displacement of beehive ovens. At the end of the war (1919), total carbonizing capacity had risen to 97 million tons per year, of which 40% was in byproduct ovens. At no subsequent time did the total capacity increase above the 97 million tons, but by 1944 almost 90% of the total capacity was in byproduct ovens. In 1962, only 2% of the total coke was produced in beehive ovens.

World War II brought imperative demands for toluene, ammonia, and other chemicals that could not be met by the coke plants. Petroleum and natural gas were used as raw materials, and since that time they have dominated. In a very real sense, the era of significance for chemicals from coal was the period from 1920 to 1940.

Let us consider now some of the most important chemicals to see how the production from coal relates to the production from other raw materials.

Ammonia

The commercial synthesis of ammonia was well established by 1925, and by 1940 had reached a production rate twice as great as the ammonia recovered from byproduct operations. From that time, byproduct ammonia held in the neighborhood of 200,000 to 250,000 tons per year until 1957. During the next five years, it dropped to about 175,000 tons per year. The production of synthetic ammonia has doubled every five or six years and by 1962 it had reached almost 6 million tons per year.

Figure 1 shows the production rate for each. Figure 2 shows the by-product ammonia as a percentage of the total. In 1962, this represented only 3% of the total ammonia production in the United States.

Benzene

Until 1950, benzene was obtained almost exclusively from the products of coal carbonization--either scrubbed from the gas as "light oil" or distilled from the tar stream. By 1940, production had risen from the depression lows to around 150 million gallons per year. During the fifties it reached a peak of almost 200 million gallons per year and has dropped significantly since. In 1950, petroleum benzene was included in the production statistics for the first time at 10 million gallons. By 1962, this had risen to 418 million gallons. Figure 3 shows the dramatic rise of this production and the relation to benzene derived from coal. Actually, much of the benzene formerly derived from coal would not be salable in today's market. It has been only by improved methods of recovery and purification that coke-oven benzene has been able to withstand the competition of petroleum-derived benzene as well as it has.

Most of the benzene produced has been used as intermediate in the manufacture of chemicals that have only come to significance since the time of World War II. Styrene, cyclohexane, and phenol account for almost three-fourths of the benzene consumption. Since 1950, the specific addition of benzene

to gasoline has been negligible in terms of the other uses. Thus it is that the recovery of benzene from petroleum sources has been in response to a demand that did not exist in the earlier days, but which is large enough so that benzene from coal could not have begun to satisfy it.

The economics of the production of benzene from petroleum sources determine the price at which benzene from coal can be sold. The coke-oven benzene production is more or less fixed by the demands of the steel industry for coke. The benzene so produced must be sold, but the production from petroleum can be flexible and can respond in volume to the price situation.

Toluene

As the demands of the first world war led to the production of toluene from byproduct ovens, so the greater demands of the second world war led to the first significant production from petroleum. During the whole history of coke-oven operation in the United States, the production of toluene from coal did not reach 50 million gallons per year. During the war, the production of toluene from petroleum in only five years rose from nothing to over 160 million gallons per year. At the end of the war, it dropped to less than 10 million gallons, then started a climb that has not yet slowed down. Figure 4 shows the production from coal and from petroleum.

The very dramatic rise during the war and sharp drop in 1946 are evidence of the flexibility of the supply from petroleum. It is this flexibility that lets the coke-oven production set a floor under the price range and the petroleum supply set a ceiling. As price increases, more and more petroleum material will come into the market--to withdraw if the price declines.

Much of the toluene produced is used for the hydrodealkylation to benzene, therefore a significant amount of benzene from petroleum is via toluene. Motor gasoline, solvents, and aviation gasoline are other major uses, and it is probably in these markets that most of the toluene from coal is used.

Xylenes

Xylenes from coal have not been of great importance in the past. During the fifties, production rose to above 10 million gallons per year for seven years, after which it dropped. Prior to World War II there was no significant production from petroleum. In 1944, almost 50 million gallons was recovered from petroleum. This dropped after the war, but in 1948 started an increase that carried production to almost 350 million gallons in 1962.

This is shown in Figure 5. A substantial part of the production is separated into the isomers for production of phthalic anhydride, isophthalic and terephthalic acids.

Phenol

The synthesis of phenol was established as a commercial practice many years ago, and by 1940 the synthetic production already amounted to three or four times the amount recovered from coke-oven operations. Phenol from coal stayed in the range of 2 to 3 million gallons per year until 1955 when it rose to 4 to 6 million gallons. Synthetic phenol has increased rather steadily from about 8 million gallons in 1940 to over 80 million gallons in 1962.

These are shown in Figure 6.

Naphthalene

Coke-oven operations have been the primary or exclusive source of naphthalene through substantially all of the period under consideration. However, some naphthalene was made from petroleum by hydrodealkylation in 1961, and by 1964 this accounted for over 40% of the total production. It has been estimated that the maximum amount available from coal tar would be approximately 650 million pounds per year. The total 1964 production (including petronaphthalene) was 740 million pounds. Obviously, future increases in naphthalene supply will necessarily be of petroleum origin.

Tar Bases

Of the tar bases, pyridine until the middle fifties was available only from coal tar, as were some of the homologs. The production of synthetic pyridine, the picolones, and others has made for a more stable market and may in the future lead to the development of more widespread uses. It is estimated that the present synthetic pyridine capacity is adequate to supply the total demand. It seems evident that, if the consumption of pyridine and other bases expands, synthetic material will supply this increase--not increased production from coal carbonization.

Coke-Oven Gas

At one period, gas was a significant byproduct of coal carbonization, too valuable to be used in underfiring the ovens. Blast furnace gas and producer gas were used for underfiring to make the coke-oven gas available for sale. In addition, a significant amount of coke was consumed in the manufacture of carburetted water gas and water gas for ammonia synthesis.

The increased availability of natural gas has substantially eliminated both of these so that coke-oven gas now finds its principal use as a captive plant fuel. Under any normal circumstances, it seems certain that future increases in fuel needs will be supplied by methane whether of natural origin or synthesized.

Coke

Coke itself, the primary product of carbonization, has experienced also the erosion of its markets by increased utilization of petroleum or natural gas. As stated above, coke for water gas production is no longer necessary to any extent. Even in the blast furnace, the use of oil or gas injection, together with other changes, has reduced the coke required per ton of iron. Many improvements in the blast furnace contributed to the reduction in coke rate, but the overall effect is striking.

In 1962, 66 million tons of pig iron were produced. At the average coke rate of 1920, this would have required over 68 million tons of coke. Actual coke usage in 1962 was only 46 million tons--a difference of 22 million tons.

Conclusions

From the foregoing, it seems evident that chemicals from coke-oven operation--no matter how important to that operation--cannot be expected to be a significant factor in the future. If chemicals from coal are to be important, they must be derived from some other means of coal conversion on a massive scale.

Work to be reported in this symposium may lead to the establishment of an industry for the conversion of coal to products such as liquid fuels on a major scale. In that case, the simultaneous production of various chemicals may be of a magnitude to challenge the dominance of petroleum and natural gas, and the income from chemicals production may be a significant part of the economic justification of such plants

In making the economic calculations, it must be remembered that in many cases the production of chemicals from petroleum is very flexible, with freedom to enter or withdraw from markets as prices fluctuate. The coal plant, presumably, will not have this freedom, and the projected chemicals income must not be calculated on the basis of a price higher than that which will induce the first petroleum competition into the market.

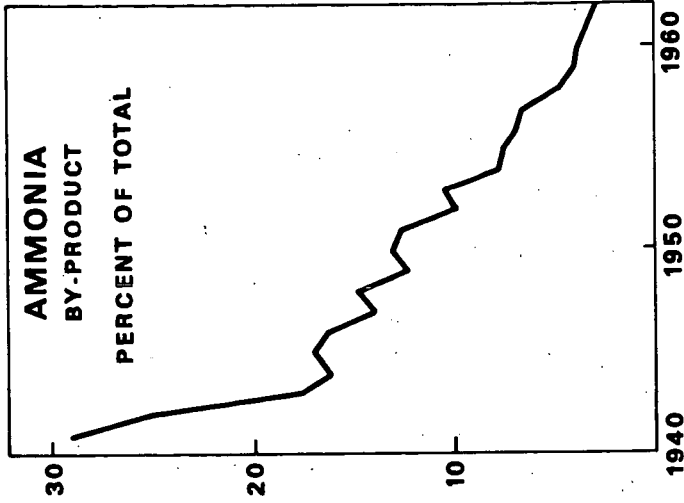


FIG. 2

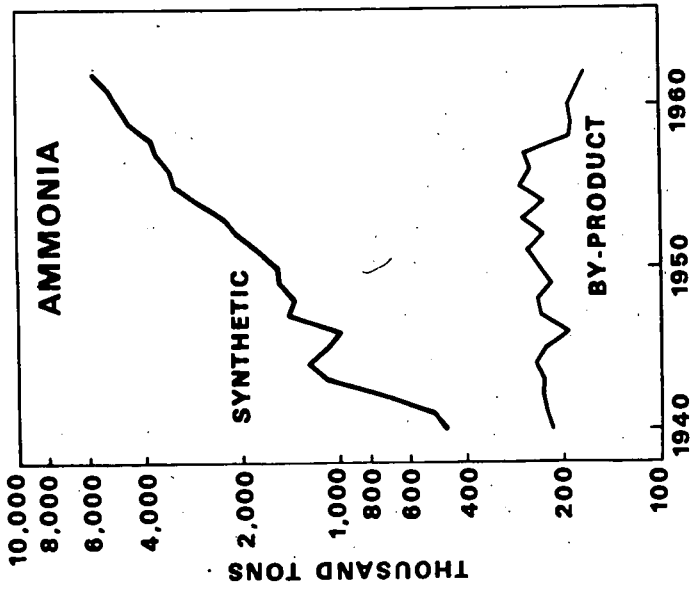


FIG. 1

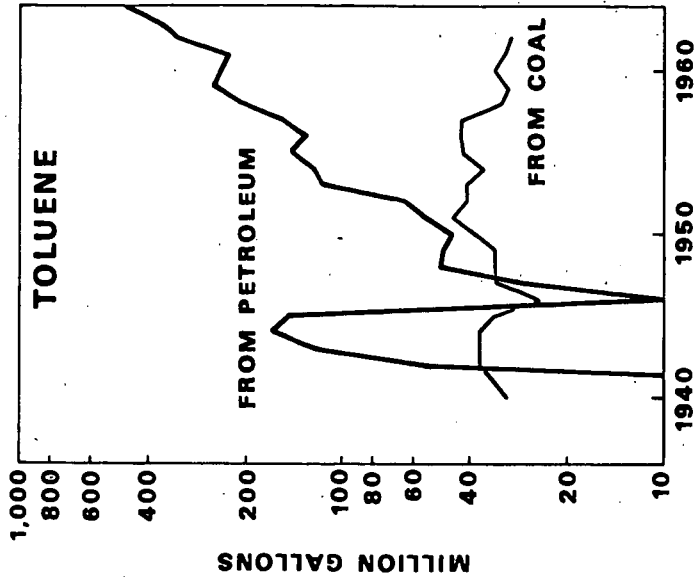


FIG. 4

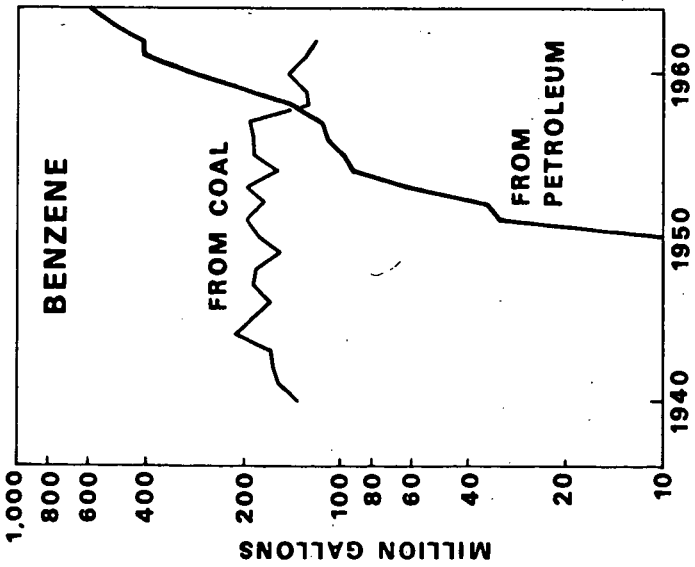


FIG. 3

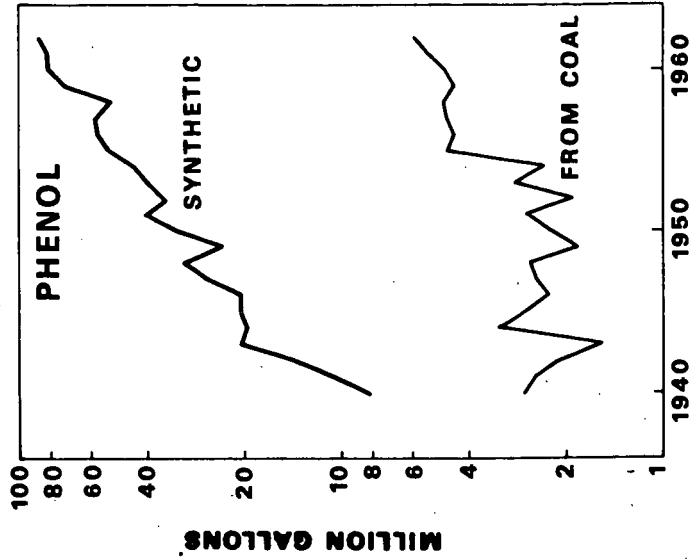


FIG. 6

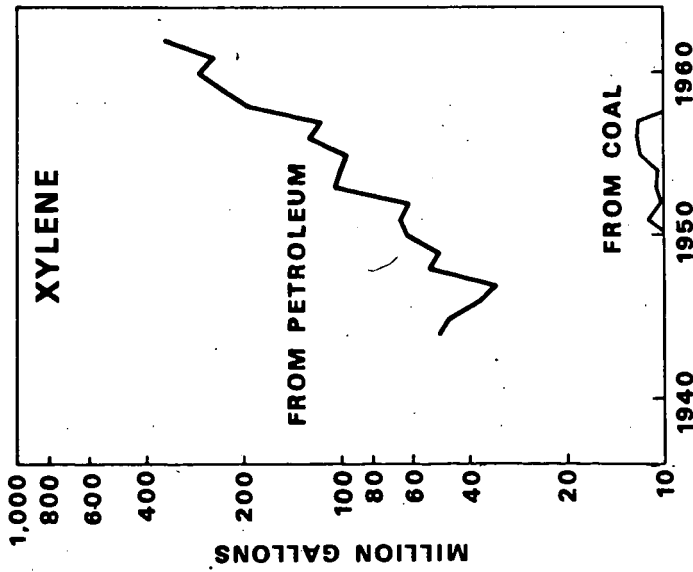


FIG. 5